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Removal of Chromium (VI) Ions from Aqueous Solution onto Micro Wave Assisted Activated Carbon Prepared from Phyillanthus Emblica Seeds

Thenmozhi M[1], Palanivel C[2]

[1]*Assistant Professor, Department of Chemistry, Krishnasamy College of Science, Arts & Management for Women, Cuddalore.*
[2]*Associate Professor, Department of Chemistry, Govt.Arts College, C.Mutlur, Chidambaram, Cuddalore. Affiliated to Thiruvalluvar University, Serkkadu, Vellore*
Email: rthen90@gmail.com

The aim of this study is to evaluate adsorption isotherms, kinetics and thermodynamic parameters of Cr(vi) ions from aqueous solutions through adsorption technique using activated carbon prepared from Phyillanthus Emblica Seeds by using Micro Wave assisted Oven. The prepared carbon designated as Micro Wave assisted Phyillanthus Emblica Seeds Activated Carbon (MWPESAC). Experiments were carried out in a batch process. Effect of pH, activated carbon dosage and contact time with different initial Cr(vi) ion concentrations were investigated. Adsorption of Cr(vi) ion from aqueous solution onto the adsorbent was investigated by taking different initial concentrations at 305, 315, 325 & 335 K temperatures. Consequences obtained from the effect of initial concentrations and temperatures were discussed in detail. Kinetic data were fitted with Lagergren, Ho and Webber –Morris equations for pseudo first order and pseudo second order and intra particle diffusion models respectively. According to Mean of Sum of Squired Error (MSSE) tool, the adsorption followed pseudo second order kinetic equation. The equilibrium data were showed with Langmuir, Freundlich, Temkin and Dubinin-Radush-Kevich isotherm equations. Implications obtained from the isotherm parameters were discussed. . Thermodynamic parameters for such as ΔH□, ΔS□ and ΔG□ were determined by means of Van't Hoff plots. Investigation of these standards inferred that adsorption was spontaneous, endothermic with increased randomness. The consequences in this study designated that MWPESAC could be employed as an adsorbent for the adsorption of Cr(vi) ions from an aqueous solution.

Keywords: Adsorption, Cr(vi) ions, Kinetics, MWPESAC, Isotherms, Thermodynamics.

1. Introduction

A toxic heavy metal ion in environment through industrial waste disposal is currently an important environmental concern. The removal of heavy metal ions from water is an essential process because they are not able undergo biodegradation and cause harmful effects to ecosystem by the accumulating in living tissues causing various diseases. Chromium is one of the most toxic heavy metal (when it leads threshold limit) to living organisms and one of the most widespread heavy metal in the environment [1-2]. Chromium is a very common substance that widely used in many industries. The potential sources of copper ion in industrial effluents include metal cleaning, plating bath, paper board, mining, anti-fouling for paint, pigment, fertilizer and wood pulp etc. [3]. The effluents usually contain high concentration of chromium ion, which has been reported that excessive intake of chromium ions in human body may leads to several mucosal irritation, hepatic and renal damage, liver and brain damages, widespread capillary damages, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney [4–6]. Among the ionic species of Chromium ions can have alarming effects in aqueous solution, attaching easily to organic and inorganic matter based on solution pH [7]. Treatment technologies available for the removal of heavy metal ions from aqueous solutions are chemical precipitation, ion exchange, coagulation and bioremediation and adsorption of all these techniques. Adsorption on solid substrate is preferred because of its high efficiency, easy handling and cost effectiveness as well as the availability of different adsorbents [8–12].

The present work is an attempt in that direction to find an alternate, cheap adsorbent. With that objective in mind, we conducted experiments to investigate the potential use of Micro Wave assisted Phyillanthus Emblica Seeds Activated Carbon (MWPESAC) for removal of Cr(vi) ions from aqueous solution.

Nomenclature	
C_i	Liquid phase initial concentrations of the adsorbate (mg/L)
C_t	Liquid phase concentrations of the adsorbate at time “t” (mg/L)
C_e	Liquid phase concentrations of the adsorbate at equilibrium (mg/L)
V	Volume of the adsorbate solutions in liter (L)
W	Mass of the adsorbent (g)
q_e	Quantity adsorbed at equilibrium (mg/g)
q_t	Quantity adsorbed at time “t” (mg/g)
T	Time in minutes
Q_e	Amount of solute adsorbed per unit weight of adsorbent (mg/g)
C_e	Equilibrium concentration of solute in the bulk solution (mg/L)
Q_0	Langmuir adsorption efficiency
B	Langmuir adsorption energy

R_L	Langmuir separation factor
C_0	Initial concentration of the adsorbate
K_f and n	Freundlich constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively
B_1	Tempkin constant related to heat of sorption (J/mol)
K_T	Tempkin equilibrium binding constant
q_D	D-R isotherm theoretical saturation capacity (mg/g)
B	D-R isotherm constant related to the mean free energy
Ε	D-R isotherm polanyi potential
E	D-R isotherm mean free energy of adsorption
R	Gas Constant
T	Temperature (K)
k_1	Rate constant of adsorption (l/min)
k_2	Second-order constants
h	Initial adsorption rate (mg/g min)
N	Number of data points

2. Materials and Methods

2.1 Preparation of Activated Carbon:

The MWPESAC carbon was prepared from Phyillanthus Emblica Seeds through Micro Wave oven. Firstly; Phyillanthus Emblica Seeds were collected and cut into small pieces. Then the materials were thoroughly mixed with different % concentration of $ZnCl_2$ solution heating at 700 W in Microwave oven for 10 minutes. After that, the found samples were wash away thoroughly with dilute hydrochloric acid (HCl) and deionized water up to the pH values reached 7.0 and finally dried at 100ºC and stored in desiccators for further studies.

2.2 Preparation of synthetic effluent:

An accurate weight of 2.8287 g (±0.0005) $K_2Cr_2O_7$ was dissolved in 1 L of distilled water to produce the stock solutions of synthetic effluent. These stock solutions were then diluted into the required concentrations using distilled water whenever necessary.

2.3 Adsorption Experiments:

Known weight of activated adsorbent MWPESAC was taken in 250 mL iodine flask and 50 mL of Chromium solution of known concentration was poured into the flask. Desired pH of the solution was brought by adding drops of dil. HCl or NaOH solutions. Then the content of the flask was agitated using rotary shaker at 130 rpm for a period of pre - determined duration. Then activated adsorbent (MWPESAC) was separated by centrifugation and the concentration of the centrifugate was determined by "Potassium Ferrocyanide" method using Double Beam UV-visible Systronics Spectrophotometer: 2202. To understand the influence of contact time on the percentage removal, experiments were carried out with the adsorbent dosage of 50 mg/50 mL and with 50 mL of Cr (vi) ions solutions of 15, 25, 35 and 45 mg/L [13].

The amount of Cr (vi) ions adsorbed in milligram per gram of adsorbent was determined by using the following mass balance equation:

$q_e = (C_i - C_e)V/W$

Where C_i and C_e are Cr (vi) ion concentrations (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in litre and m is the weight of the adsorbent in grams. The percentage of removal of Cr (vi) ions was calculated using the following equation:

Removal (%) = $(C_i - C_e)/C_i$ x 100

3. Result and Discussion:

3.1 Effect of Contact time and initial concentration:

The effect of contact time on percentage removal of metal ions for different initial concentration have been shown in figure.1. Adsorption of metal ions from the solution increases with the time and finally attains equilibrium in 60 minute for the initial concentrations of adsorbate 15, 25, 35 and 45 mg/L respectively. The percentage of removal increased with the increase in contact time and decreased with the increase of initial concentration of the metal ions. However the amount of metal ions adsorbed on the adsorbent increased with the increase of initial concentration of the metal ions solution. The percentage of removal of metal ion and amount of metal ion adsorbed were given in table:1.

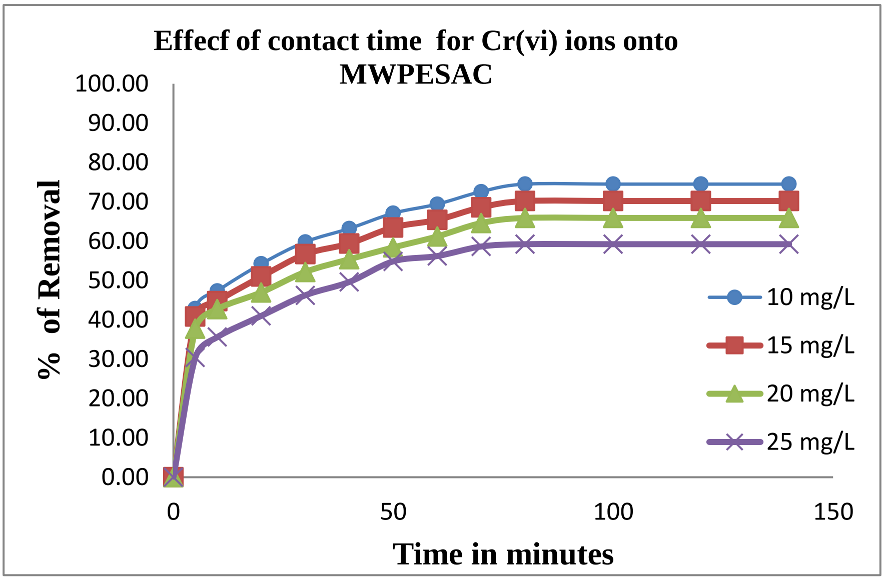


Figure: 1

Table: 1 Percentage of removal of metal ion and amount of metal ion adsorbed

C_i (mg/L)	% of Removal of metal ion at equilibrium	Adsorbed amount of Cr(vi)ion at equilibrium (mg/g)
10	74.50	07.45
15	70.20	10.53
20	65.90	13.18
25	59.23	14.81

3.2 Effect of pH:

The pH of the adsorbate solutions has been identified as the most important parameter governing sorption of adsorbates on different adsorbents. This is partly due to the fact that hydrogen ions themselves are a strong competing sorbate and partly to the fact that the influence on the chemical speciation of adsorbates. The effect pH of solution was studied by taking pH of the adsorbate solution from 2 to 12.

The effect of pH on the percentage removal of solute from the aqueous phase was found to be varied for different solutes for the same adsorbent depending upon the nature of the solute.

Figure.2 shows that the Cr(vi) ions highest removal efficiency was attained at pH 2. Cr(vi) ions generates negative charged metal ions when dissolved in water. When the pH is lower than pH_{zpc}, the charge on the surface of the adsorbent is positive. At very low pH, the positive charge accumulates on the surface of the adsorbent and facilitates more adsorption of dye anions. Moreover at low pH, the concentration of OH^- ions was very meager. Hence the competition for the positively charged cite by OH^- ions will be low. When the pH of the solution is raised the positive charge on the surface decreases with the increase in OH^- ions concentration. The OH^- ions being smaller in size preferentially adsorb and render repulsive force towards the approaching metal anions. Hence the adsorption of Cr(vi) ions was low at higher pH of the solution[14].

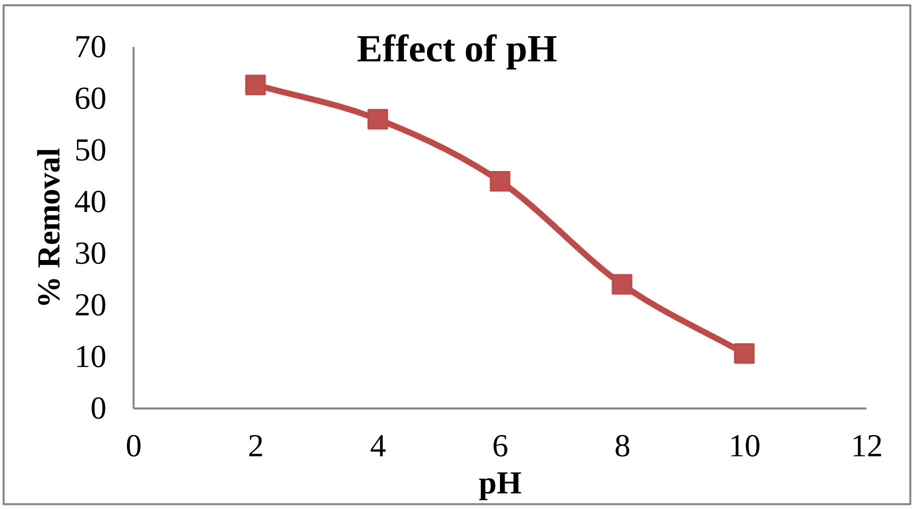


Figure: 2

3.3 Effect of Temperature:

It is well known that temperature plays an important role in the adsorption process. The metal ions removal increase rapidly from 305, 315, 325 and 335 K this result suggests that the experimental temperature had a greater effect on the adsorption process implying that the surface coverage increased at higher temperatures were shown in figure: 3. This may be attributed to the increased penetration of metal ions inside micro pores or the creation of new active sites at higher temperatures. This indicates the endothermic nature of the controlled adsorption process. Similar result has been reported in the literature [15].

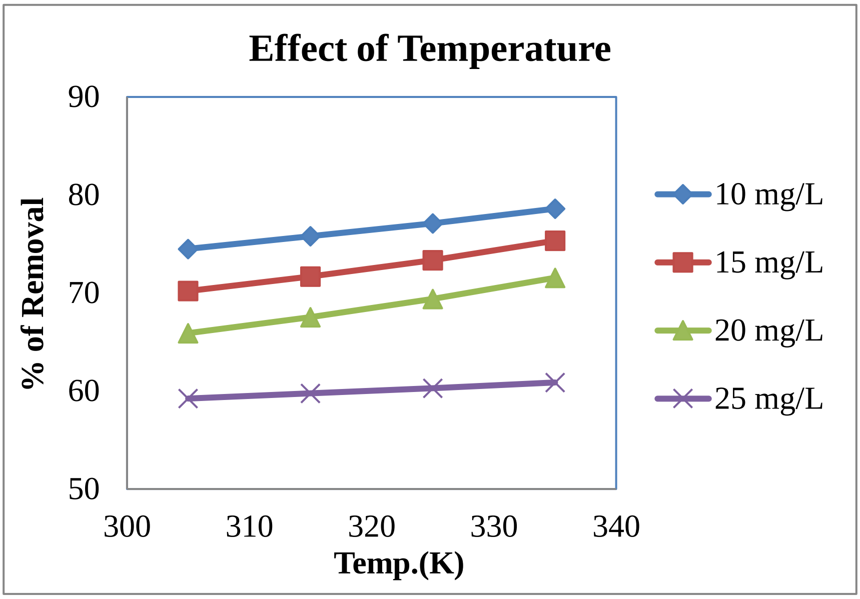


Figure: 3

4. Adsorption Kinetics:

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. Plots of different kinetic models applied were given in the Figure: 4 and the kinetic parameters calculated were given in the Table: 2. Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as its R^2 values were very close to unity. Moreover, difference between qe (cal) and qe (exp) values of second order is small when compared to first order kinetic model. Statistically it is tested with the tool Sum of error squares (SSE%) [16]. The Δqe and SSE % values were given in the Table: 3 from which it was concluded that second order kinetic model was more appropriate rather than first order kinetic model.

Table: 2 Data processing Tools

S. No.	Parameters		Formulae
1.	Kinetic Models & SSE %	Pseudo First order kinetics (Legergren equation)	$\log (q_e - q_t) = \log q_e - k_1/2.303 \times t$
		Pseudo Second order kinetics (Ho equation) The initial adsorption rate	$t/q_t = 1/k_2.q_e^2 + 1/q_e\ t$ $h = k_2 q_e^2$
		Sum of error squares	SSE (%) = $\surd\sum[(q_e)_{exp} - (q_e)_{cal}]^2 / N$
2.	Isotherms	Langmuir Separation factor	$C_e / Q_e = 1/Q_0 b + C_e / Q_0$ $R_L = 1 / (1 + b\ C_0)$
		Freundlich	$\log Q_e = \log K_f + 1/n \log C_e$
		Tempkin	$q_e = B_1 \ln K_T + B_1 \ln C_e$
		Dubinin – Raduskevich, Polanyi potential Mean free energy of adsorption	$\ln q_e = \ln q_D - B\varepsilon^2$ $\varepsilon = RT \ln (1 + 1/C_e)$ $E = 1/(2B)^{½}$
3	Thermodynamics	Gibbs Equation Van't Hoff equation Std. Free energy	$\Delta G = - RT \ln K_L$ $\ln K_L = - \Delta H/RT + \Delta S/R$ $\Delta G° = \Delta H° - T\Delta S°$

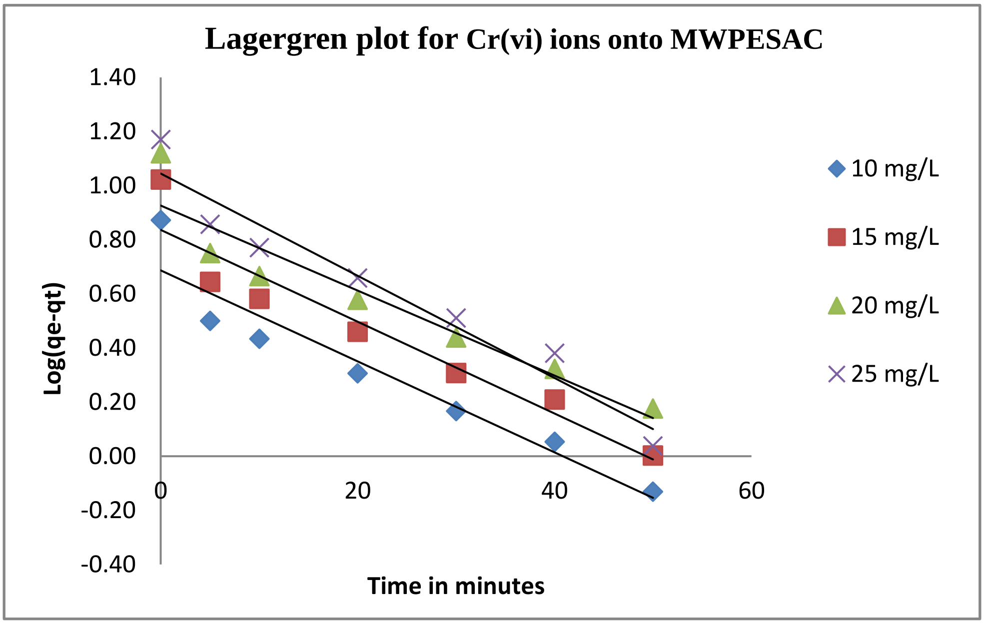


Figure: 4

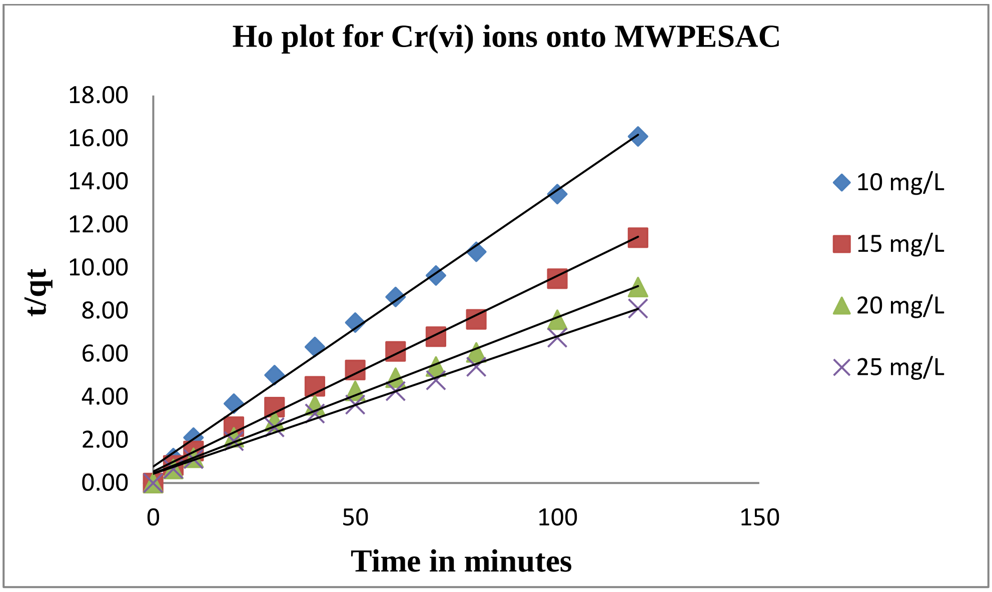


Figure: 5

Table: 3 Kinetic parameters for Cr(vi) ions onto MWPESAC

Ci mg/L	Rate constants		$q_{e(cal)}$ mg/g		$q_{e(exp)}$ mg/g		Δq_e		R^2		(SSE %)	
	k_1 (10^{-2}) (min^{-1})	k_2 (10^{-3}) $(gmg^{-1} min^{-1})$	First Order	Second order	First order	Second Order	First order	Second Order	First order	Second order	First order	Second Order
15	0.0362	0.0215	8.4431	7.7882	7.45	7.45	0.99	0.11	0.8944	0.995	2.33	0.30
25	0.0387	0.0154	4.8641	11.0011	10.53	10.53	32.10	0.22	0.9132	0.992		
35	0.0394	0.0117	6.8628	13.7931	13.18	13.18	39.91	0.38	0.9119	0.994		
45	0.0435	0.0095	11.0866	15.6495	14.81	14.81	13.84	0.71	0.943	0.9938		

5. Adsorption Isotherm Studies:

The existence of equilibrium between the liquid and solid phase is well described by adsorption isotherms. Equilibrium data collected at different temperatures were fitted in Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich adsorption isotherm models [17]. These isotherms are depicted in Figure: 5 to Figure: 9. The R^2 values of these isotherm plots reveal that Freundlich isotherm well describes the present system that is the possibility of multilayer adsorption. R^2 value of Dubinin-Raduskevich isotherm is very low. In Dubinin-Raduskevich isotherm, the very low value of the constant ‘B’ related to the mean free energy of adsorption per mole of the adsorbate and the adsorption is physical in nature. Results of various isotherms are presented in Table: 4.

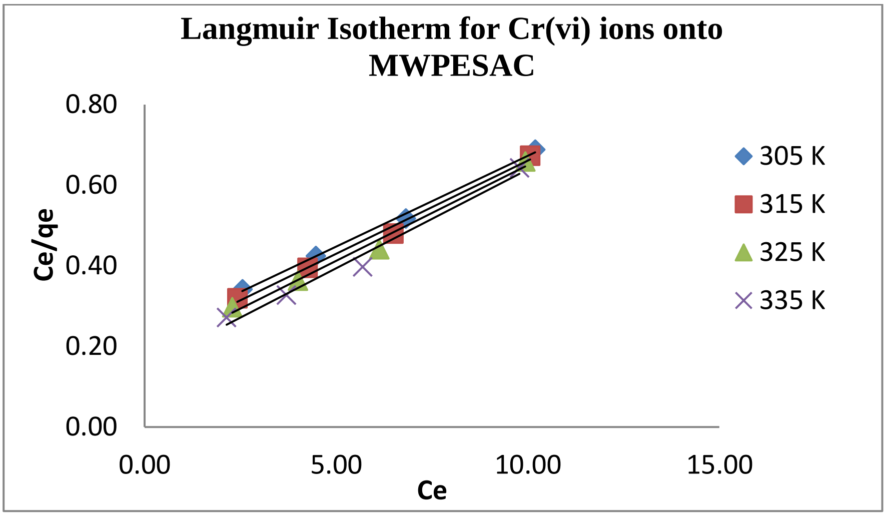
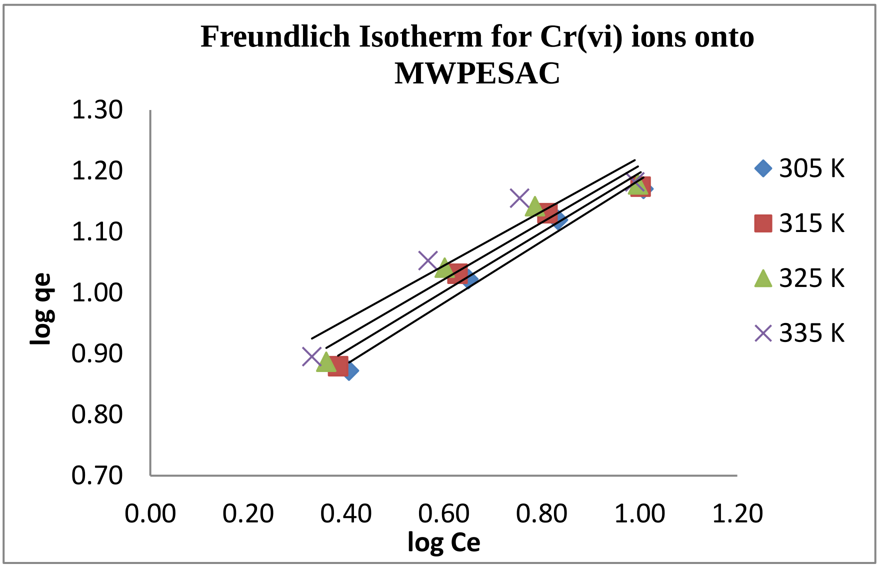


Figure: 6



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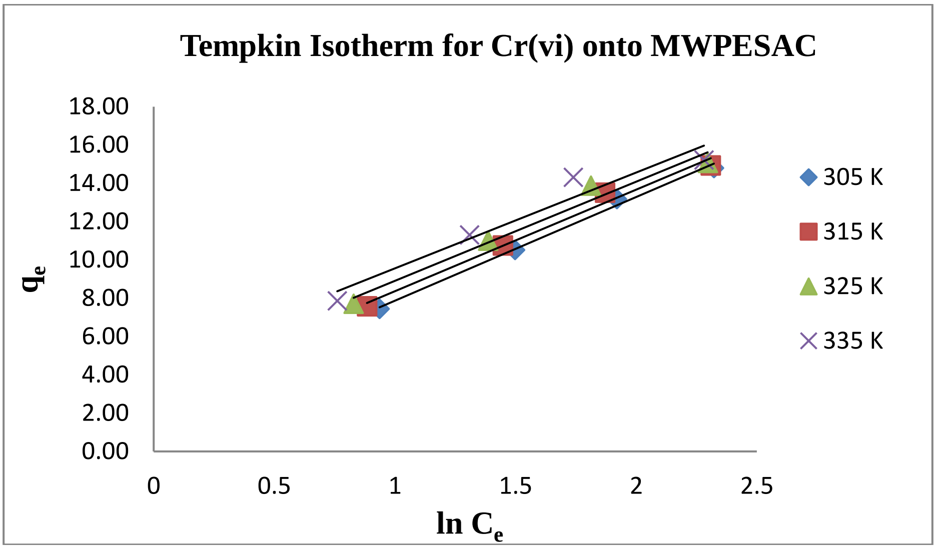

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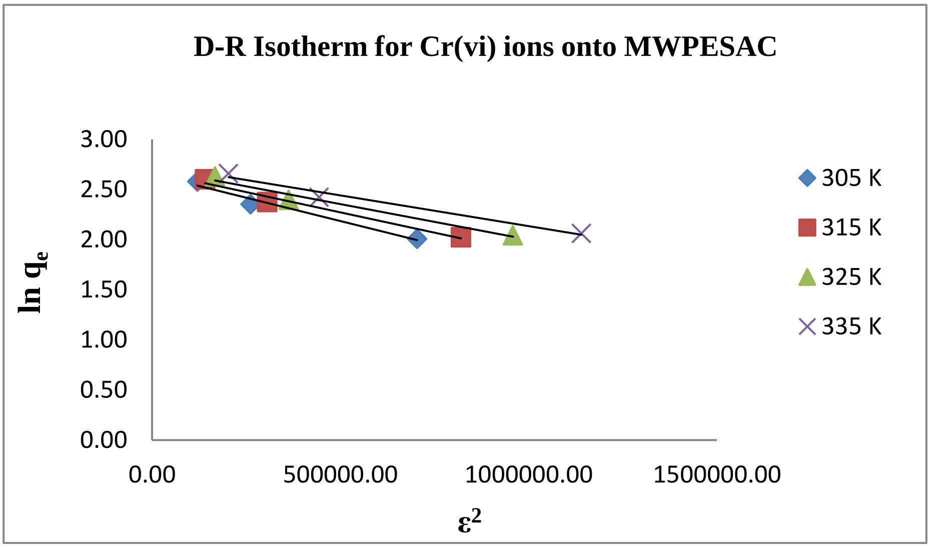

Figure: 9

Table: 4 Results of various isotherms plots for the adsorption of Cr(vi) ions onto MWPESAC

Isotherms	Temp	Parameters and their results			
	(K)	Q_0 (mg/g)	b	R_L	R^2
Langmuir	305	20.408	0.202	0.331	0.9967
	315	21.053	0.232	0.301	0.9927
	325	21.645	0.271	0.269	0.9873
	335	22.222	0.329	0.233	0.9817

Freundlich		n	k_f (mg/g^{-1})		R^2
	305	1.9822	4.7929		0.9792
	315	2.0555	5.1298		0.9660
	325	2.1395	5.5132		0.9446
	335	2.2548	6.0034		0.9127
Tempkin		B_T (J/mg)	a_T (L/g)		R^2
	305	468	1.574		0.9948
	315	493	1.782		0.9859
	325	521	2.055		0.9691
	335	556	2.485		0.9408
Dubinin Raduskevich		q_D (mg/g)	E (kJ/mol)	$B \times 10^{-4}$ (mol^2/J^2)	R^2
	305	522.63	0.6033	2.6510	0.9726
	315	560.52	0.6076	2.6767	0.9721
	325	607.19	0.6112	2.7090	0.9737
	335	644.73	0.6142	2.7478	0.9770

Analysis of Isotherm:

Langmuir isotherm:

In the present study Q_m value ranges from 20.408 to 22.222 as the temperature increases the monolayer adsorption capacity also found to increase. This kind of results were obtained in various similar studies [18]. The separation factor R_L values in between 0 to 1 indicates the favourable adsorption. R^2 values of isotherm ranged between “0.9817 to 0.9967”

Frendlich isotherm:

The values of n were between 1 and 10 which indicates cooperative adsorption. The R^2 values were close to unity which reached to good fitting into frendlich isotherm [19].

Temkin Isotherm:

b_T - Temkin constant is related to the heat of adsorption. This b_T value increased from 468 to 556 as the temperatrue of adsorption increased. The temkin parameter a_T value give on idea about nature of adsorption. In our present study the a_T values ranged from 1.574 to 2.485 which indicate the adsorption is physical nature. The R^2 value was low compared to langmuir and frendlich isotherm [20].

Dubinin-Raduskevich:

The activation energy E value ranges from 0.4875 to 0.4833 and adsorption capacity q_D value from 522.6292 to 644.7318 indicates the physisorption. The R^2 value was very low when compared to other three isotherms. In general the fitting data in isotherm equation were in the following order Langmuir > Temkin > Dubinin-Raduskevich > Frendlich [21].

6. Thermodynamic of adsorption

Thermodynamic limits designed since van't hoff plot are assumed in Figure: 10 & Table: 5. Negative standard free energy of adsorption designates that the adsorption method is reasonable and spontaneous in nature. The endothermic nature of adsorption is confirmed by the positive ΔH° values. The bonding amongst Cr(vi) ions and MWPESAC superficial is very weak, since ΔH° values are found to be in amongst 1.92 to 7.42 kJ/mol. Positive values of ΔS° recommended respectable attraction of the metal to the adsorbent and the adsorption is spontaneous in nature [22-24].

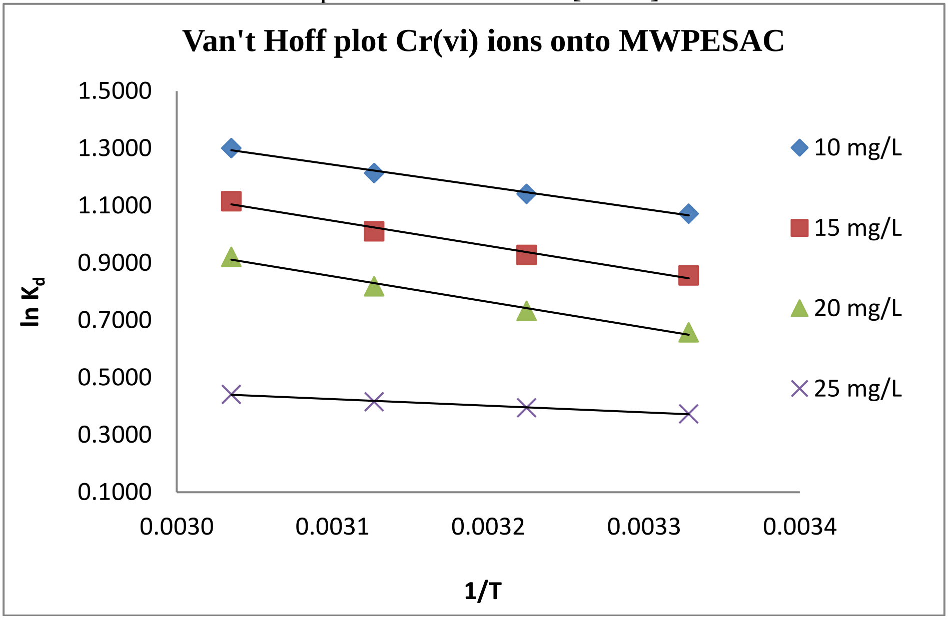

Figure: 10

Table: 5 Thermodynamic Parameters for Cr(vi) ions onto MWPESAC

C_i (mg/L)	Temperature (K)	k_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K)
15	305	2.9216	-2.7191	7.42	29.94
	315	3.1322	-2.9907		
	325	3.3668	-3.2808		
	335	3.6729	-3.6241		
25	305	2.3557	-2.1731	7.31	30.99
	315	2.5294	-2.4308		
	325	2.7500	-2.7339		
	335	3.0541	-3.1101		
35	305	1.9326	-1.6710	6.43	29.96
	315	2.0817	-1.9204		

	325	2.2680	-2.2131		
	335	2.5149	-2.5691		
45	305	1.4528	-0.9472	1.92	9.40
	315	1.4845	-1.0348		
	325	1.5170	-1.1262		
	335	1.5556	-1.2309		

7. Conclusion:

The present investigation shows that MWPESAC is an effective adsorbent for the removal of Cr(vi) ion from aqueous solutions. From the kinetic studies, it is observed that adsorption of Cr(vi) ion is very rapid in the initial stage and decreases while approaching equilibrium. The equilibrium time increases with initial concentration. The percentage removal of Cr(vi) ion increases with the increase in adsorbent dosage and decreases with increase in initial concentration. Experimental results are in good agreement with Langmuir isotherm when compared to other three isotherm models. Adsorption of Cr(vi) ion obeys pseudo-second order equation with good correlation. Thermodynamic parameters such as ΔH^o, ΔS^o, ΔG^o values inferred that the adsorption was spontaneous, endothermic and physical nature.

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